

# PYROLYSIS KINETICS OF THE WASTE-TIRE CONSTITUENTS: EXTENDER OIL, NATURAL RUBBER, AND STYRENE-BUTADIENE RUBBER

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## ABSTRACT

In order to design tire pyrolysis and combustion processes, it is helpful to know the kinetics of thermal decomposition of tires. In this study, pyrolysis kinetics of tire constituents are reported. A thermogravimetric analyzer, coupled with a Fourier-Transform Infrared spectrometer for gas-product analysis, was used in a series of non-isothermal pyrolysis experiments. The heating rates were 1 K/min, 3 K/min, 30 K/min, and 100 K/min. The results are discussed in terms of single and distributed activation energy kinetics, and a comparison with the available literature data is made.

## INTRODUCTION

It has been demonstrated by several studies that, to some degree, the decomposition of the organic part of tires can be related to the decomposition of its separate components, i.e., extender oil, natural rubber (NR), butadiene rubber (BR), and styrene-butadiene rubber (SBR) [1-3]. There exists, however, appreciable uncertainty about the value of the activation energy ( $E$ ) corresponding to each decomposition process; a wide variation in the observed values of activation energies has been reported by several investigators [2-5]. Whether the differences between the results of various studies arise from differences in tire material components, experimental set-ups used, or methods of activation-energy determination is unclear, and we shall try to shed some light on this issue in this study.

In general, previous investigators used single activation energies which, in some cases, were found to vary with the heating rate [3,4].

## KINETIC ANALYSIS

In what follows, it is implicitly assumed that the reaction rates to be determined follow first-order kinetics, which is a reasonable starting assumption for the polymers used in tires. While isothermal techniques are useful to determine kinetic parameters, their implementation is time-consuming. Non-isothermal techniques provide faster means to obtaining this kinetic information. The most common non-isothermal technique is the so-called Friedman method [6], in which the logarithm of the rate constant,  $k$ , is plotted at each point as a function of the inverse temperature. The rate constant,  $k$ , is calculated from the equation:  $dw/dt = k(w_f - w)$ , where  $w$  is the sample weight at time  $t$ , and  $w_f$  is the final sample weight. Since  $k$  is equal to  $A \exp(E/RT)$ , ( $A$  is the pre-exponential factor,  $E$  is the activation energy,  $T$  is temperature in degrees Kelvin), the parameters  $A$  and  $E$  can be determined from the linear region(s) of the plot of  $\ln(k)$  versus  $1/T$ . A drawback of this method is the fact that it introduces a bias in the values of  $A$  and  $E$  when the reaction has a distribution of activation energies [7]. In such a case, the Friedman method is unable to differentiate between the effect of the distribution and the effect of the magnitude of the mean activation energy, and gives an erroneous value for the mean value of  $E$ . This value is usually lower than the "true" value [7].

Another non-isothermal method of determining the kinetic parameters involves the measurement of the temperature at which the rate of volatile evolution is maximum,  $T_{max}$  [5,8]. This technique was used in this study. The method has been shown to be applicable to the determination of  $E$  and an approximate value of  $A$  for wide distributions of activation energies [7]. In a typical sequence of experiments, thermal-decomposition rates are measured at different heating rates. The relationship between the heating rate,  $M$ , and the value of  $T_{max}$  is given by the following equation

$$\ln(M/T_{max}^2) = \ln(A/E) - E/(RT_{max}),$$

from which the kinetic parameters  $A$  and  $E$  can be determined [8]. While the value of  $E$  is accurately determined even for wide distributions, the value of  $A$  usually requires a slight adjustment (typically within a factor of two) [7]. The width of the distribution,  $\sigma$ , can then be determined from the width of the peak representing the rate of weight loss. In the  $T_{max}$  method, some difficulties can be encountered when peaks are not well resolved; in such cases, substantial shifts in  $T_{max}$  can occur. However, the same problem arises when using the Friedman method, unless deconvolution of the peaks is attempted [4]. Another limitation is associated with the presence of small, multiple maxima superimposed on a broader peak, i.e., when the assumption of the first-order kinetics is not fully supported. In this case, again, the applicability of both the  $T_{max}$  and Friedman methods is limited. The exact value of  $T_{max}$  may also be difficult to determine for large, broad peaks.

In the present study, the  $T_{max}$  method was employed, and an attempt was made to reduce the limitations of the  $T_{max}$  method by using: 1) a large number of heating rates; 2) very low heating rates for the improved peak resolution; and 3) in the case of noisy data, the measurement of  $T_{max}$  was made at the mid-point of the peak width in order to minimize the effect of noise on  $T_{max}$ .

## MATERIALS AND EXPERIMENTAL

Samples of extender oil, natural rubber, polybutadiene rubber and poly-styrene-butadiene rubber were obtained from Pirelli-Armstrong, New Haven, Connecticut, and a sample of scrap-tire material was provided by Oxford Tire, Plainfield, Connecticut.

The weight loss and volatile-species evolution were monitored throughout the thermal decomposition of the sample using the TG-FTIR apparatus and technique described previously (a thermogravimetric analyzer coupled with a Fourier-transform infrared spectrometer for volatile-species analysis; see references [9,10]). Sample sizes used varied between 10 and 20 mg. The tire particles were sieved to  $20 \times 40$  mesh. The following heating rates were used in the TG-FTIR experiments: 1, 3, 10, 30, 100 and 200 °C/min. In other thermogravimetric studies of tire pyrolysis, the heating rates were varied only by a factor of 6–50, with the data often reported for just one tire component. Thus, with regard to the range of the heating-rate variation and the number of tire components studied, our work seems to be most comprehensive to date.

## RESULTS AND DISCUSSION

In general, TG-FTIR experiments showed that at least 90% of the weight loss was attributable to tar, the remaining 10% being  $H_2O$ ,  $CO$ ,  $CH_4$  and  $CO_2$ . It was found that the gases evolved approximately in the same temperature range as the tar did, which is in agreement with our previous work [5]. In view of this result, it was decided that a comprehensive analysis of the gas-species evolution was unnecessary, and the value of  $T_{max}$  was determined from the weight-loss data. The rate of weight loss as a function of temperature is shown in Figure 1 for oil, NR, BR, and SBR heated in helium at 30 °C/min.

The  $T_{max}$  method was applied to the TG data for extender oil, NR, BR and SBR, as shown in Figure 2, where  $\ln(MT_{max}^2)$  is plotted as a function of  $1/T_{max}$ . Wherever possible, the available literature data have been expressed in terms of  $\ln(MT_{max}^2)$  and  $1/T_{max}$ , and they are included in the plot. It can be seen that the  $T_{max}$  method applies reasonably well to the experimental data, and fairly linear trends are obtained. It can be concluded that the activation energy, as determined using the  $T_{max}$  method, appears to be constant over the range of heating rates used. This result is in contrast with the study by Williams and Besler [3], in which the variation in the activation energy with the heating rate was reported when the Friedman method was employed.

It should be noted that only limited accuracy in the values of  $T_{max}$  reported in the literature is expected as  $T_{max}$  was not meant to provide kinetic information there, but was merely used as an approximate index of reactivity. In most studies, the Friedman method was utilized to determine the pyrolysis kinetics. The slight differences observed in Figure 2 between the data of this study and the literature data may be caused by several factors, including the use of somewhat different materials, differences in the temperature measurement, and differences in the way  $T_{max}$  was determined. A summary of the kinetic data obtained in this study is shown in Table 1.

Interpretation of the data for the extender oil presents an inherent difficulty associated with the accurate determination of  $T_{max}$  because the decomposition covers a wide range of temperatures. However, even with a significant uncertainty for  $T_{max}$  of  $\pm 7$  K, i.e.,  $1/T_{max} \sim \pm 0.015 \times 10^{-3} \text{ K}^{-1}$ , the kinetics of this process can be estimated (see Figure 2a and Table 1). It seems particularly appropriate to use the  $T_{max}$  method to determine the pyrolysis kinetics for this material as a distribution of activation energies is likely to occur in the case of oil components having different molecular weights. If applied, the Friedman method would grossly underestimate the value of  $E$ , and the determined kinetics would apply only to a narrow range of heating rates. In fact, the literature values of the activation energy have been reported much lower than the value determined in this study (e.g.,  $E/R = 5.9 \times 10^3$  K reported by Yang *et al.* [2] versus  $E/R = 10 \times 10^3$  K found in this study). Using the activation energy determined by the  $T_{max}$  method, the value of  $\sigma$  (the width of the distribution) was found by fitting the Gaussian-distribution model to the experimental data. The width of the Gaussian distribution function is reported in Table 1.

In Figure 3, the predicted and experimental oil-decomposition patterns are shown for two different heating rates. Predictions were made using both single- and distributed-activation-energy models.

In the single-activation-energy model, a value of  $E/R = 5.9 \times 10^3$  K was used, as reported in reference [2]. The pre-exponential factor was adjusted to provide the best fit for the low-heating-rate data (Figure 3a). It can be observed that the distributed-activation-energy kinetics fit the data at both heating rates, whereas the single-activation-energy model fails at the high heating rate (Figure 3b).

The activation energy found for natural-rubber decomposition (Table 1) appears consistent with literature data [2,3,11–14]. Also,  $T_{max}$  values from the literature data are relatively similar (Figure 2b). From the shape of the decomposition peak (in particular the width of the peak) as a function of temperature, it was found that a single activation energy would fit the data fairly well.

The uncertainty in  $T_{max}$  for the NR has been estimated to be  $\pm 3$  K, i.e.,  $1/T_{max} \sim \pm 0.007 \times 10^{-3} \text{ K}^{-1}$ . In Figure 4, thermal-decomposition data are shown for two heating rates, as well as model predictions made using the kinetics derived from the  $T_{max}$  analysis. Good agreement between the data and model predictions can be seen. Data in Figure 4 also imply a change in the reaction mechanism that occurs between the low heating rate and the high heating rate. At the low heating rate (Figure 4a), a shoulder is observed at high temperatures, which is not present in the high-

heating-rate data (Figure 4b). This most likely represents the presence of a residue which forms only at the low heating rate, and which is more stable than the original rubber material. The residue readily decomposes at higher temperatures.

Previous studies showed that the decomposition of BR occurs in a two-step process: (1) depolymerization; followed by (2) the decomposition of the residue [15]. This behavior can also be observed in this study, since two weight-loss peaks were observed, as shown in Figure 5. It can also be seen in Figure 5 that the decomposition behavior changes with the heating rate: at the low heating rate, the low-temperature peak (related to depolymerization) is insignificant compared to the high-temperature peak (the residue-decomposition peak). At high heating rates, however, the low-temperature peak (depolymerization) becomes larger, and can account for as much as 50% of the weight loss. This change of mechanism occurs over a relatively narrow range of heating rates (1 to 100 °C/min), and illustrates the difficulty in the kinetic analysis applied within a range of process conditions. In previous studies [15, 16], the activation energy for the depolymerization process was reported, while this work provides values for the process of residue decomposition. The  $T_{max}$  data for the butadiene rubber (the residue-decomposition peak) appear in Figure 2c, and they show a fair agreement with the studies carried out under similar conditions. In particular, the three high-temperature points from the work by Williams *et al.* [3] lead to an activation energy similar to the one found in the present study. The difference observed with the low-temperature point may result from the fact that, in the present study, the  $T_{max}$  was measured at the mid-point of the peak width, slightly below the peak maximum, while it is not known how it was measured by Williams *et al.* This detail is particularly important because the BR peak is not completely "smooth," and exhibits some shoulders that were neglected here in order to provide more reliable kinetics. In addition, differences between various types of BR may account for the observed discrepancy.

As seen in Figure 1, the SBR decomposition occurs over a wide temperature range, with "shoulders", and is probably not accurately represented by a single activation energy. It is then expected that the  $T_{max}$  method (as well as any method based on the assumption of a single activation energy reaction) provides only approximate values for the kinetic parameters. As seen in Figure 2d, two values of  $T_{max}$  are reported, the main one referring to the center of the main peak, and the other to the shoulder observed in the weight-loss derivative curve, prior to the main peak. It can be seen in Figure 2d that the literature data fall along either one of the two curves. This result suggests that different types of SBR may have been used, which decompose differently depending, for example, on the methods used in rubber synthesis or on the co-polymer composition. The data from Figure 2d were used to determine activation energies that are shown in Table 1. Similar values of  $E/R$  were obtained by applying the  $T_{max}$  approach to our data and to the data of other investigators ( $E/R = 35\text{--}40 \times 10^3$  K). These values are found to be high compared to the literature values determined using the Friedman method with the assumption of a single activation energy ( $E/R = 17\text{--}25 \times 10^3$  K). Clearly, the assumption of a single activation energy is in this case inadequate. The thermal decomposition of SBR appears to involve a number of chemical reactions, i.e., a model with distributed activation energies is more appropriate. The  $T_{max}$  method may then be more accurate since it does not make any assumption about the width of the distribution. However, the large uncertainty in the value of  $T_{max}$  ( $\pm 7$  K, i.e.,  $1/T \sim \pm 0.015 \times 10^{-3} \text{ K}^{-1}$ ), which is due to the wide and complex decomposition peak, leads to a large uncertainty in the activation energy.

## CONCLUSIONS

The activation energy for the decomposition of oils, NR and BR was found to be independent of the heating rate. This result is in contrast to the results of some studies which found a variation of the activation energy with the heating rate. It is believed that this discrepancy is a result of the different kinetic analyses performed (the  $T_{max}$  method versus the Friedman method). It appears that a widening of the peak may occur at high heating rates, which would result in a lower activation energy determined by the Friedman method, whereas the value obtained from the  $T_{max}$  method would be unaffected.

A distributed activation energy was found to be more appropriate for the description of oil decomposition as compared with a single-activation-energy model.

A single-activation-energy model adequately describes the decomposition of NR and the BR residue. However, SBR decomposition cannot be easily represented by a single-activation-energy process. The SBR decomposition peak seems to consist of three components, and further work on the kinetic analysis of this peak is needed.

Changes in thermal-decomposition mechanisms have been identified for BR and NR pyrolysis. Caution is advised in extrapolating the kinetics to the heating rates appreciably different from the ones used in kinetic experiments.

The kinetics of waste-tire pyrolysis and its relationship with the kinetics of individual tire components will be a subject of a separate paper.

## ACKNOWLEDGMENT

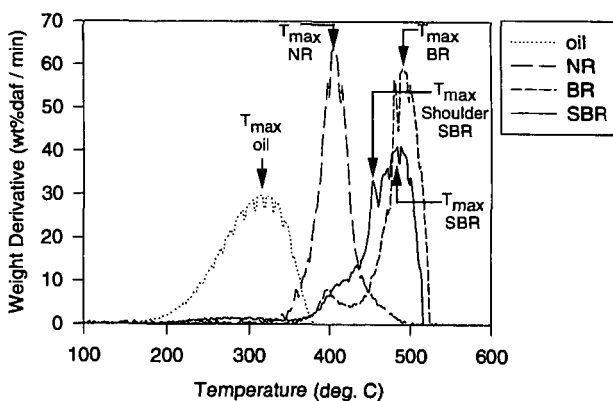
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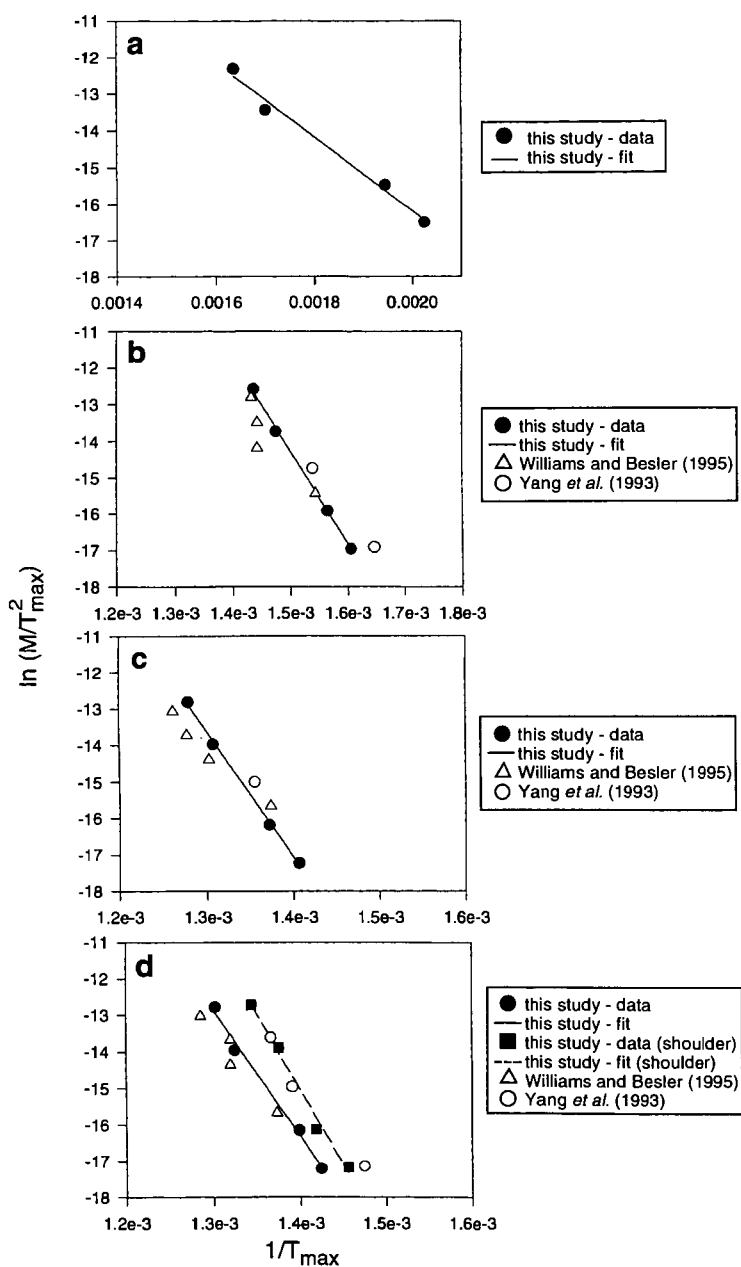
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**Table 1** The kinetic parameters for the thermal decomposition of tire components: extender oil, natural rubber (NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR).  $E$  is the activation energy,  $R$  is gas constant,  $A$  is the pre-exponential factor and  $\sigma$  is the width of the Gaussian distribution function.

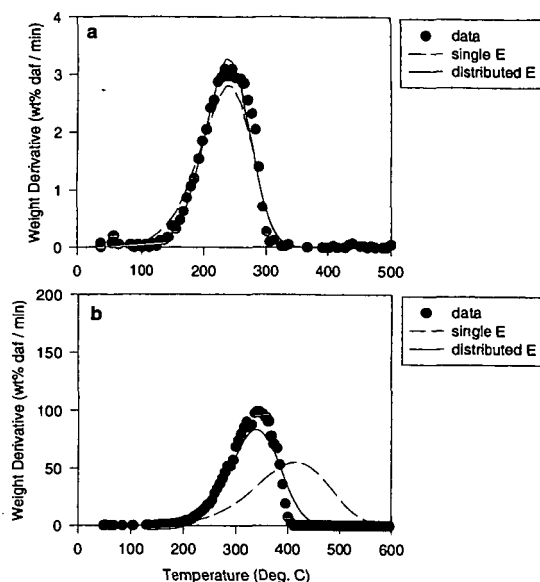
Material/Peak	$E/R \times 10^{-3}$ (K)	$A$ ( $s^{-1}$ )	$\sigma/R \times 10^{-3}$ (K)
extender oil	10	$5.2 \times 10^5$	0.5
NR	25.6	$8.2 \times 10^{14}$	0
BR: 1st peak 2nd peak	23 $\rightarrow$ 76 34.4	$1.15 \times 10^{18}$	0
SBR: main peak shoulder	35.1 40.1		



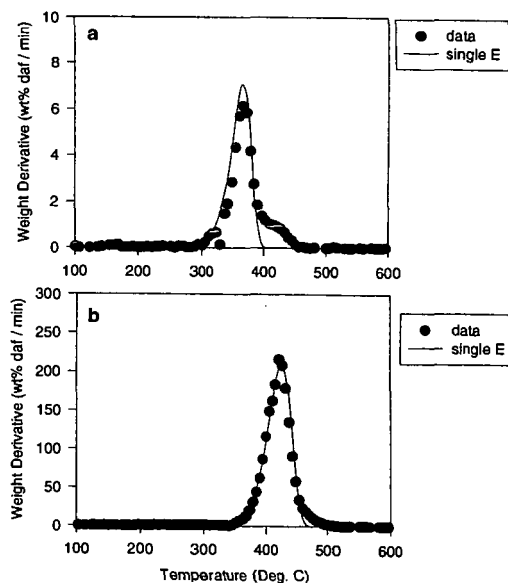
**Figure 1** Rate of weight loss from the TGA experiment for extender oil, natural rubber, butadiene rubber and styrene-butadiene rubber.



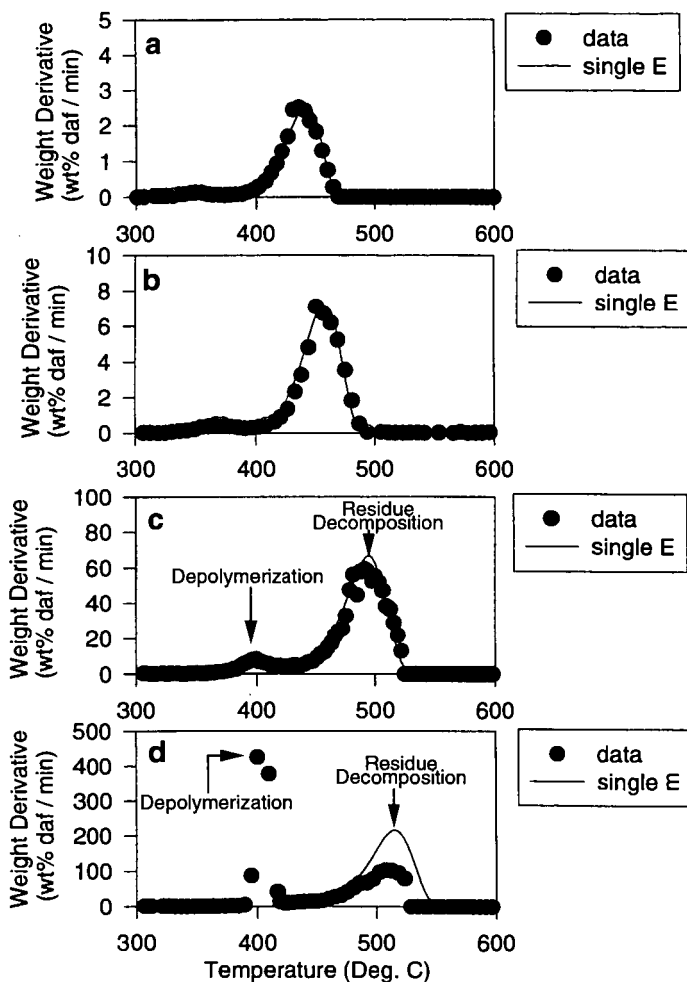
**Figure 2** Determination of kinetics using the  $T_{\max}$  method for a) extender oil, b) natural rubber, c) butadiene rubber, and d) styrene-butadiene rubber. The figure includes data from this study as well as literature data [2,3].



**Figure 3** The comparison of data and model predictions for the decomposition of oils at a) 3 °C/min; and b) 100 °C/min. The solid lines represent predictions made by using a distribution of activation energies. The value of the mean activation energy was taken from Table 1, and the width of the distribution was fitted to match the data. The dotted lines represent predictions made by using a single activation energy and the pre-exponential factor that was adjusted to fit the 3 °C/min data.



**Figure 4** The comparison of data and model predictions for the decomposition of natural rubber at a) 3 °C/min; and b) 100 °C/min. The solid lines represent predictions using a single activation energy, the value of which was taken from Table 1.



**Figure 5** The comparison of data and model predictions for the decomposition of butadiene rubber at a) 1 °C/min; b) 3 °C/min; c) 30 °C/min; and d) 100 °C/min. The solid lines represent predictions made by using a single activation energy, the value of which was taken from Table 1. The low-temperature peak corresponds to depolymerization, while the high-temperature peak corresponds to the decomposition of the residue.